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Corrosion susceptibilities of various metals and alloys in synthetic geothermal brines

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The corrosion susceptibilities of various pure metals and alloys were investigated in synthetic geothermal fluids. Rates of corrosion of AISI 1010 steel, types 304 and 316 stainless steels, Monel 400 and nickel were determined at three temperatures (296, 333 and 368 K); and those of the molybdenum, niobium and titanium were determined at 368 K only. Type 304 stainless steel appears to undergo an active–passive transition at a temperature range between 333 and 368 K. In the passive state type 304 steel has essentially the same corrosion rate as type 316. At 368 K the corrosion rate of pure nickel was approximately 2.5 times that of Monel, which in turn was twice that of type 316 stainless steel. The corrosion rates of Mo, Nb and Ti were less than one mdd at the highest experimental temperature.

1. Introduction

The assessment of material behaviour has become one of the most important considerations in proposed schemes for the utilization of various forms of geothermal energy. Because of the severity of geothermal environments, problems associated with corrosion and scaling have become major obstacles in the way of harnessing this form of energy. In the Salton Sea Trough of Southern California and Northwest Mexico the volume of brine with > 570 K temperature, estimated to be about 3×10^{10} m^3, represents a significant source of energy [1]. Unlike previously reported geothermal brines [2], the Salton Sea fluids have higher dissolved salt concentrations (up to 30%) and low pH values (~3) [3]. At the time this work was initiated no experimental information was available concerning the behaviour of materials in such an environment. Recently, however, Carter and Cramer [4] published results of a corrosion study of commercial metals and alloys in synthetic brines representing those of the Salton Sea geothermal wells.

This paper gives the result of an investigation of the corrosion behaviour of AISI 101 steel, stainless steels 304 and 316, Monel 400, nickel, molybdenum, titanium and niobium in a synthetic geothermal brine in the temperature region between room temperature and ~370 K.

2. Experimental materials and methods

A synthetic solution designed to simulate reported Salton Sea brines [3] was made by dissolving appropriate amounts of NaCl, KCl and $CaCl_2$. Regardless of temperature these salts were completely soluble in the appropriate volume of distilled water. To obtain the desired pH of ~3, hydrochloric acid was added to the solution and in doing so it was possible to maintain a pH level between 2.5 and 4 at all times. Variations in the pH values of such a magnitude were commonly observed between similar wells in the geothermal fields of the Salton Sea region. No data concerning the concentration of dissolved oxygen in the actual brines were available. Although no specific attempt was made to maintain a given level of oxygen concentration in the synthetic solutions, measurements before and after even the longest test gave values between 8 and 10 ppm oxygen. In comparison to other work [4], the synthesized brine simulates those of the high-salt fluids of the Niland wells.

The materials tested in this work were AISI 1010 steel, 304 and 316 stainless steels, Monel

400, 99.9% pure nickel and 99 +% pure samples of Mo, Nb and Ti. Coupons of 5.08 cm x 2.54 cm were sheared from sheet stock and a 0.95 cm diameter hole was punched at one end of each for all materials except titanium which was machined and drilled. Each coupon was punched with identifying marks, thoroughly wet-sanded with 240 grit carbimet paper, rinsed with distilled water, degreased by rinsing with acetone and dried with hot air. Each coupon was then weighed on an analytical balance capable of differentiating 0.0001 gram. The corrosive medium was held in a glass jar 15.2 cm high and 15.2 cm in diameter. Glass hooks were used to suspend the corrosion coupons completely immersed in the brine. An iron–constantan thermocouple in a thin glass shield filled with distilled water was attached to the Plexiglas lid and suspended in the brine to measure the brine temperature. Continuous monitoring of the temperature was maintained with a stripchart recorder. Tests were conducted at 296, 333 and 368 K.

This assembly was situated inside a similar jar 25.4 cm high and 25.4 cm in diameter by means of a stainless steel rod support. A copper sheathed immersion heater was coiled to a diameter of 17.1 cm and positioned so as to uniformly surround the brine container. This heater and a thermoswitch were attached to a Plexiglas lid fitted to the 25.4 cm diameter jar. The thermoswitch was wired in series with the immersion heater and a variac power supply. In this configuration the brine container was surrounded by a distilled water bath. This entire two-jar assembly was located inside a third glass jar 30.5 cm high and 30.5 cm in diameter and surrounded on all sides by 2.5 cm of fibreglass insulation. This apparatus configuration made it possible to control brine temperatures to a maximum deviation of ± 1.5° C. Provision for stirring was not provided and a typical ratio of fluid volume to sample area of around 90 was maintained.

Prior to an experimental run the corrosion apparatus was allowed to come to thermal equilibrium at the desired test temperature. Nine coupons were initially inserted into the apparatus. After the first desired duration, three coupons were removed and the pH of the solution readjusted. The exposed coupons' macroscopic appearances were noted after which the surfaces and edges of each were mechanically and chemically cleaned in accordance with standard procedures [5]. Each coupon was again rinsed with acetone, dried with hot air, weighed and recorded. This procedure was repeated removing three more coupons for each of the remaining durations. Occasionally the cleaning procedure was repeated to check the effectiveness of the scale removal. At no time was there more than a 0.0002 g difference between the weights before and after the second cleaning. Visual and microscopic observations were made before and after the removal of the corrosion products.

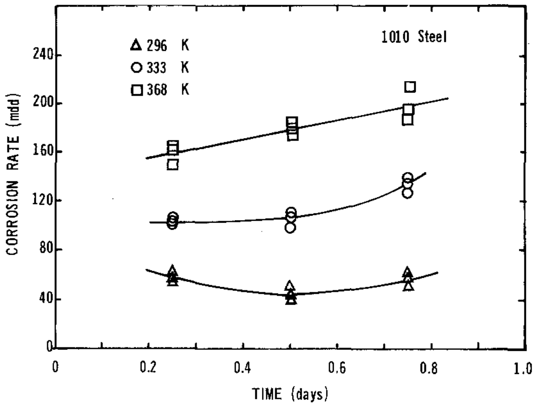

Figure 1 Corrosion rates of AISI 1010 steel.

3. Results

Corrosion rate versus duration graphs for all materials except molybdenum, niobium and titanium are depicted in Figs. 1 to 5. For the three latter metals, corrosion rates were low even at the highest test temperature, 368 K. Fig. 6 is representative of the average rates and the scatter in the data for these metals. All rates reported here are average values for the duration of the test.

Maximum corrosion rates at all temperatures at the 95% confidence level are presented in Table I.

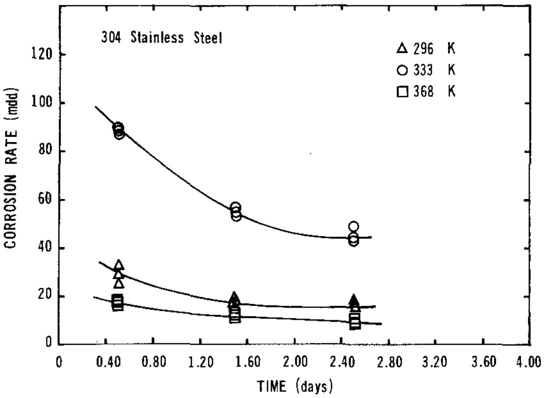

Figure 2 Corrosion rates of type 304 stainless steel.

TABLE I Maximum corrosion rates and macroscopic appearance

Material	Maximum corrosion rate (mdd) (95% confidence level)			Maximum test duration (days)	Macroscopic appearance at maximum duration and $T = 368$ K
	368 K	333 K	296 K		
AISI 1010 steel	236.89	147.70	67.79	0.75	Nonadherent heavy black scale. Approx. 100% coverage.
304 SS	11.03	53.21	18.31	0.50	Very adherent light grey scale. Approx. 90% coverage (296 and 333 K approx. 5–10% coverage).
316 SS	9.81	9.20	8.59	2.00	Very slightly adherent gold tarnish along edges.
Monel 400	21.73	11.66	5.53	2.50	Nonadherent heavy grey-black scale. Approx. 80% coverage.
Nickel	55.25	29.42	6.37	2.00	Very adherent heavy grey scale. Approx. 100% coverage.
Molybdenum	0.57	–	–	7.00	Very adherent blue discoloration. Approx. 90% coverage.
Niobium	0.43	–	–	8.00	Very adherent light grey scale. Approx. 80% coverage.
Titanium	0.16	–	–	7.00	Very adherent gold tarnish. Approx. 80% coverage.

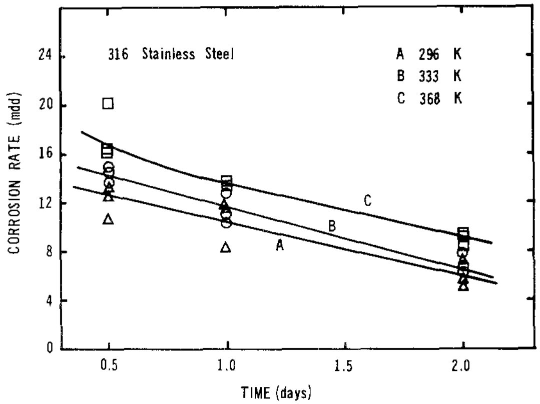

Figure 3 Corrosion rates of type 316 stainless steel.

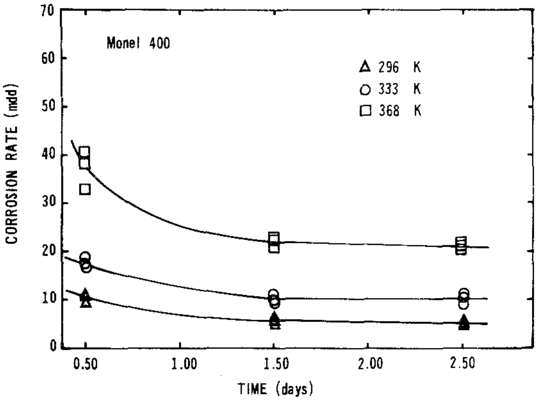

Figure 4 Corrosion rates of Monel 400.

These values were calculated from the upper limits of the 95% confidence intervals on the true mean of the specific weight loss. Also presented in Table I are descriptions of the macroscopic appearance of the samples after maximum exposure at the highest temperature. Particularly adherent scales such as those on the nickel samples could not be removed as thoroughly as the nonadherent scales on e.g. AISI 1010 steel or Monel. Thus, the reported corrosion rates for Ni represent lower limits for this metal.

4. Discussion

Despite the build-up of a heavy black scale, weight loss measurements on the 1010 steel showed no tendency for passivation. The detrimental influence of NaCl, KCl and $CaCl_2$ solutions on the corrosion rates of plain carbon steels is well documented [6, 7]. Furthermore, the corrosion of such steels [8] experiences a dramatic increase as the pH decreases to about 4. An active–passive transition is observed for the 304 stainless steel at a temperature between 333 and 368 K. The curve representing the corrosion rate versus time at 368 K lies below that representing the 296 K data. Observation of passivation for this steel has been previously reported [9]. Increased NaCl concen-

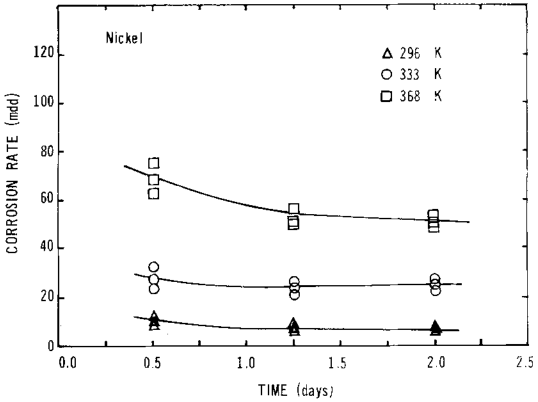

Figure 5 Corrosion rates of nickel.

tration decreases the temperature at which passivation commences [10]. For an 18-8 steel which is virtually identical to the 304 steel of this study, the transition temperature in 10% NaCl solution was observed to be approximately 353 K. In the present study scale formation was clearly evident at the higher temperatures, 368 K, and essentially absent at lower temperatures.

Stainless steel type 316 exhibited passive behaviour at all test temperatures. The small magnitudes of weight loss values and the experimental scatter associated with them make it difficult to discern a temperature influence on the corrosion rate of this material. The corrosion rates of the passive state of the 304 steel (at 368 K) are essentially the same as those of the 316 at all temperatures. Carter and Cramer [4] reported no measureable rate of corrosion for a 316L stainless steel immersed 15 days in a de-aerated Salton Sea brine at 305 K. At 378 K and under a 1 atm pressure, the corrosion rate for this steel was reported to be 22.17 mdd in the aerated high-salt (Niland brine) for the same duration of time. In the low-salt (Holtville brine) this steel showed no sign of corrosion at 378 K during a 15 day test in both aerated and de-aerated solutions.

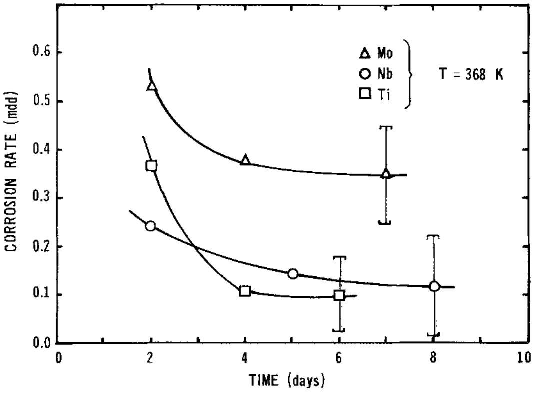

Figure 6 Average corrosion rates for molybdenum, niobium and titanium.

The results on Monel show a relatively strong dependence of the corrosion rate on temperature in the range 296 to 368 K. The corrosion rate at 368 K is nearly a factor of four higher than that at 296 K. Carter and Cramer [4] report a corrosion rate of 21.5 mdd for Monel 400 at 378 K in an aerated high-salt brine. This compared to a value of 21.73 mdd determined at the highest temperature (368 K) of this study. A similar temperature dependence of the corrosion rate is evident from the results of the authors mentioned above. When the test temperature was increased to 305 K, the corrosion rate of Monel 400 was approximately 123 mdd. Regardless of temperature, the corrosion rates of Monel appear to approach a constant value with increasing exposure time, Fig. 4. This apparent tendency to passivate is associated with the formation of a non-adherent black scale. In such a case and in others with non-adherent scales, exposure to a moving brine could remove the protective films and thus result in an increased corrosion rate. However, if the corrosion process is diffusion controlled, increased velocities can enhance the stability of the passive state. There is evidence that Monel behaves in such fashion in sea water [11].

The corrosion of nickel exhibits a stronger dependence on temperature than that observed for Monel. At 296 K the corrosion rate of nickel is roughly 10% higher than that of Monel. However, at 368 K nickel corrodes at a rate exceeding 2.5 times that for Monel. As indicated previously, the corrosion products formed on nickel were difficult to remove and thus it is believed that the reported corrosion rates represent lower limits for this metal.

Molybdenum, niobium and titanium exhibited outstanding corrosion resistance in the synthetic brine. Because of the relative stability of these metals, corrosion rates were determined only at the highest test temperature. Under these conditions, molybdenum and niobium corrosion rates are less than 0.6 mdd and that for titanium was approximately 0.2 mdd. The results of Carter and Cramer indicate a zero rate at 378 K under all conditions of aeration and salt concentration. At a higher temperature, 305 K, titanium experiences a slight (< 3 mdd) general corrosion, but a severe 15 mdd pitting corrosion.

Because of the relatively short test duration of this study, lack of observation of pit formation cannot, of course, be considered as a significant result. Incubation periods of significantly longer times may be required to assess the severity of pitting corrosion in geothermal brines. The pH of these solutions is at the lower limit of the range in which 18-8 steels exhibit pitting corrosion [12] in a 4% salt solution at 363 K.

Acknowledgement

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